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Intensification of biodiesel production via ultrasonic-assisted process: A critical review on fundamentals and recent development

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ABSTRACT

Biodiesel is a good alternative fuel to petroleum diesel. It is produced through transesterification reaction between vegetable oil or animal fats and alcohol. The process faces various problems related to the immiscible nature of the reactants causing poor mass transfer rate. This drawback is responsible for long reaction time and low reaction rate leading to an energy intensive process. Process intensification through the use of active catalyst, pressure reactor, high temperature, high stirring rate or even non-conventional approaches such as supercritical method and Biox process often subjects to drawbacks with respect to energy consumption, product quality and reactants cost. This paper highlights recent development in the production of biodiesel under ultrasonic irradiation conditions. It handles the drawback of poor immiscibility between reactants as ultrasonic energy can emulsify the reactants to reduce the catalyst requirement, reaction time and reaction temperature. Ultrasonic energy also neglects the limitations in the use certain feed stocks. Fundamental aspects of the ultrasonic-assisted process using homogeneous and heterogeneous catalysts are reviewed. Recent achievement and future development in this technology in a batch and continuous process are also highlighted.

Contents

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1. Introduction

The depletion of fossil resources and environmental pollution are among the most critical problems that threat humanity. The attention is currently turned towards the use of biomass or biomass-derived materials as replacements to petroleum fuel. In 1893, Rudolf Diesel attempted to make use of peanut oil as fuel for diesel engine [1]. During 1930s and 1940s, vegetable oils replaced diesel fuels in many events, usually in emergency cases. In August 1982, the first international conference was held to discuss the use of vegetable oils as fuels. Many topics were highlighted including the cost of fuel, plausible methods of manufacturing, the characterizations of the fuel and the effects of fuel derived from vegetable oil on the efficiency of diesel engines [2]. These bio oils look promising to replace petroleum fuel but technical hurdles are still lying ahead.

Biodiesel is a mixture of mono alkyl esters with long-chain fatty acids that is derived from vegetable oils or animal fats [3]. It has many good properties compared to diesel fuel. It is an eco friendly fuel and biodegradable. Besides being non toxic, it is mainly free of sulfur components and aromatics [4]. Biodiesel can mix at any percentage with petroleum fuel or it can itself be used as a successful fuel [5].

There are four different methods to produce biodiesel from bioresources. Direct use and blending of raw oils are among the early approaches where vegetable oils are used directly or diluted with petroleum diesel to run the engine [6–9]. Micro-emulsions which is colloidal equilibrium dispersion of optically isotropic fluid usually form spontaneously from two normally immiscible liquids [10]. Thermal cracking that is the conversion of triglycerides to biofuel with or without the presence of catalyst is another approach and it involves the use of high temperature in the absence of air or oxygen [11,12]. As the process in an energy-intensive one, limited success has been achieved in such approach.

Recently, transesterification has been actively investigated as the most popular way to convert vegetable oils or animal fats into fatty acid methyl esters (FAME) [13]. Fig. 1 illustrates the general equation of transesterification reaction [14]. It is the organic reaction that causes the exchange of organic group (R″) of an ester with the organic group (R′) of an alcohol where, R1, R2, R3 are long-chain hydrocarbons, usually called fatty acid chains. The main types of fatty acids in vegetable oils and animal fats are such as palmitic, myristic, stearic, oleic, linoleic and linolenic. Typical compositions of various oils are shown in Table 1. Transesterification mechanism consists of a series of consecutive reversible reactions. Triglyceride molecules react step by step with methanol to form diglyceride, monoglyceride and in the last step, glycerol is formed (Fig. 2).

One mole of FAME is generated in each step of the transesterification process [15]. All of these reactions are reversible and essentially the goal in this reaction is to shift the equilibrium to the products side, forming more fatty acid esters and glycerol. Usually, methanol is used in the biodiesel production process as it is relatively cheap compared to other alcohols and has small chain of carbon. However, as of the reaction is reversible, excess alcohol is needed to shift the reaction to form more products [16]. This reaction is commonly catalyzed by acid or base catalysts while another possibility could be through the use of enzymatic catalyst (biocatalysts) especially lipases.

Biodiesel production process has undergone significant progress in recent years with some innovations introduced to improve efficiency and productivity. Due to recent emergence of ultrasonic-assisted technology for biodiesel production with reported benefits as compared to conventional production process, mature understanding o this topic is deemed necessary. As such, this review aims at improving the understanding of ultrasonic phenomena and their effects on biodiesel production process to meet specific requirements in the process. Reported behaviors in various processes used for biodiesel production are properly analyzed and reviewed.

2. Demands in biodiesel production process

A wide range of studies have been dedicated to the production process of biodiesel using various methods and some of them could achieve good yield and look promising for large scale

$$TG + CH_3OH \underset{k2}{\overset{k1}{\rightleftharpoons}} DG + FAME$$

$$DG + CH_3OH \underset{k4}{\overset{k3}{\rightleftharpoons}} MG + FAME$$

$$MG + CH_3OH \underset{k6}{\overset{k5}{\rightleftharpoons}} GLY + FAME$$

Fig. 2. The sequence of transesterification reaction.

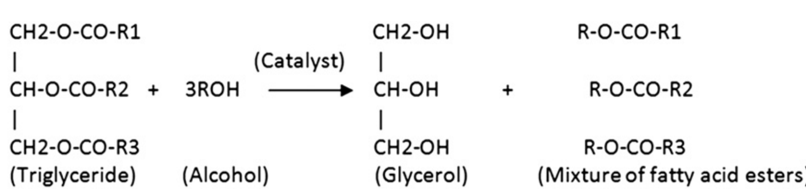


Fig. 1. General-glyceride transesterification to biodiesel.

Table 1
Typical fatty acid composition of various oil sources.

Name	Structure	Formula	Composition (wt.%)					
			Palm	Soybean	Cottonseed	Coconut	Rapeseed	Tallow
Lauric	12:0	$C_{12}H_{24}O_2$	0.1	0.1	0.1	46.5	–	0.1
Myristic	14:0	$C_{14}H_{28}O_2$	1.0	0.1	0.7	19.2	–	0.8
Palmitic	16:0	$C_{16}H_{32}O_2$	42.8	0.2	20.1	9.8	3.5	23.3
Stearic	18:0	$C_{18}H_{36}O_2$	4.5	3.7	2.6	3.0	0.9	19.4
Oleic	18:1	$C_{18}H_{34}O_2$	40.5	22.8	19.2	6.9	64.1	42.4
Linoleic	18:2	$C_{18}H_{32}O_2$	10.1	53.7	55.2	2.2	22.3	10.7
Linolenic	18:3	$C_{18}H_{30}O_2$	0.2	8.6	0.6	–	8.2	0.4

production. Some researchers focus their study on the economic aspects of the process with respect to the types of feed stock, their availability and price that could influence the economy of the process [17]. Fig. 3 that shows the distribution of biodiesel production cost. The main contributor to overall cost of the process is the feed stock (the vegetable oil or animal fats) while the second one is the chemicals that are used in the reaction such as the catalyst and alcohol. In the transesterification process, excess alcohol is commonly used to shift the equilibrium towards the formation of the methyl esters. In this respect, it should be mentioned that catalyst reusability is almost impossible if homogeneous catalyst is used. The development of methods for the production should focus on the reduction of these costs. The investment of cheap recourses of triglyceride and efforts to reduce the amounts of the chemicals used should also be considered. These days, some researchers are actively investigating the enhancements on the process to eliminate or reduce these problems or drawbacks. The aim is always to produce the desired product at an optimum rate while at the same time possesses high quality while at the same time demonstrates good process economy [18].

The enhancements in biodiesel production are generally aimed at generating high quality biodiesel that conforms to international standards such as ASTM or EN standard. One of the approaches is to minimize the quantity of side products or at least to minimize the side reactions [19,20]. High quality biodiesel can be used in diesel engine without any negative effects while at the same time can generates less pollutants to environment [21].

In the other hand, new technology should reduce reaction time needed for the reaction and lower the reaction temperature. These parameters could affect the product quality as the feed stock (vegetable oil or waste cooking oil) can undergo various side reactions at high temperature, especially when long reaction time is needed. Operating a system with high temperature does require huge amount of energy. As such, process improvement towards achieving sharp reduction in reaction temperature is deemed necessary. The reduction in the energy consumption is expected to improve the energy ratio (output energy/input energy) leading to better net energy to be obtained from biodiesel. For example, energy ratio for biodiesel produced from palm oil was found to be 3.53, indicating a net positive energy production [22]. In future, production process with even lower energy input should have a positive influence if sustainable energy supply were to be considered.

Working in a safe environment demands the use of low reaction temperature because of low boiling point of methanol. The risks of exposure to its vapor will be less and the need for a closed system in order to control the evaporation and temperature will be eliminated [23]. Closed systems often require extra control mechanism on the pressure and the need for special equipment design that will have great influence on production costs. Besides, as the products are not continuously removed from the reaction system, equilibrium will be shifted to the reverse reaction especially at high conversion. Thus, the production process should be ideally carried out at atmospheric pressure.

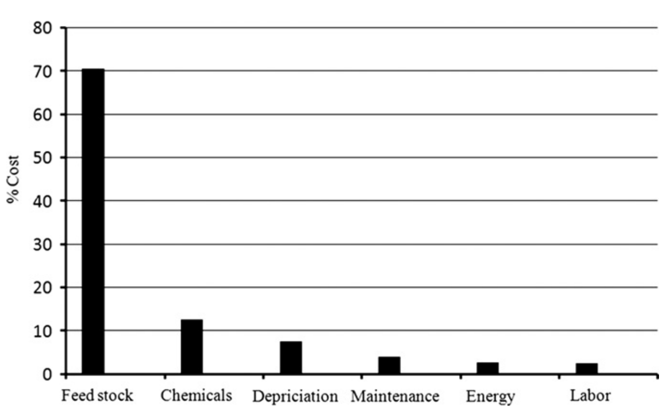


Fig. 3. Costs of biodiesel production [19].

The development of a new technology for biodiesel production should consider the effects on the desired catalyst. It is necessary to find an operating procedure that allows optimum catalytic activity to reduce the catalyst amount to be used. This factor is important as the reduction in the quantity of catalyst will reduce the level of purification step for the product. That will lower the cost of the whole process by reducing the process time to produce the final product [24]. At the same time, better quality of biodiesel will be achieved as some components of the catalyst could leach into the biodiesel [7]. In this study, the main drawbacks and recent development in the production process of biodiesel is critically reviewed. This report also highlights recent topics that receive attention among researchers when attempting the intensification of biodiesel production process.

3. Main drawbacks in biodiesel production process

In biodiesel production through transesterification, serious problems and limitations can be identified. First of all, the immiscible nature of the reactants (alcohol and vegetable oil) coupled with the difference in their densities can lead to poor contact between the reactants. Consequently, reduction in mass transfer rate results loading to low reaction rate and increased reaction time [25]. The reaction between two immiscible fluids is analogous to the heterogeneous transport phenomena (heat, mass and fluid) that are caused by the lag in the film between them. The transport could be accelerated by many ways such as by increasing the driving force including decreasing the thickness of the film or changing some physical properties. The best way that can be applied in this problem is film mixing and it can be achieved by many strategies like vigorous agitation [26,27] or by the application of ultrasonic energy [20].

The biodiesel production process can actually be carried out in two ways i.e. with or without the use of catalyst. The catalyzed production can be divided into homogenous and heterogeneous reactions. For this purpose, strong acid or base catalysts are possible to be used but the latter type is significantly more active. Homogenous reaction systems generally record high yield [28,29]. The drawback of base catalyzed systems is the limitation in the use of several oil feed stocks because of their sensitivity to the presence of free fatty acids (FFA) in the oil. Amounts of FFA larger than 1 wt% will react with the base catalyst to form soap according to the reaction equation as shown in Fig. 4 leading to loss of the catalyst from the system [13]. The soap also complicates the product purification process to leading to a significant increase in overall production cost. Even with low FFA, base homogenous catalysts itself are hard to be removed from the product and requires two or three times of washing with hot water [30].

Homogenous acid catalysts are relatively less active compared to base catalysts but they have no sensitivity towards FFA. Thus, the reaction using these catalysts must be maintained at high temperature but the biodiesel yield in the process could be low. These drawbacks translate into high production costs and low

$$\underset{\text{FFA}}{\text{R-COOH}} + \underset{\text{Catalyst}}{\text{KOH}} \longrightarrow \underset{\text{soap}}{\text{R-COOK}} + H_2O$$

Fig. 4. General equation for soap formation [13].

productivity. Besides that, acidic catalyst is corrosive and destructive to the reactor and other supporting equipment involved in the process [31]. Current focus is therefore shifting towards the use of heterogeneous catalysts which are considered more environmental friendly.

Heterogeneous catalysts can achieve high biodiesel yield [32] and have no tendency to be affected by high content of FFA. For that reason, no foam will be generated and the need for extra purification process is eliminated. Consequently, higher purity of biodiesel and glycerin is obtained. All of these benefits will lead to better economy of the production process [33]. Despite all these advantages, biodiesel yield that is obtained with heterogeneous catalyst is still relatively lower than that of homogenous catalysts. It is therefore a conventional approach to increase the yield by increasing the reaction temperature and pressure. As a result, the production cost is higher even with the use of cheap feed stocks while the net energy obtained from the biofuel is reduced [34].

Despite positive influence in accelerating the biodiesel production process, there are several serious drawbacks that are associated with the use of catalysts. Therefore, mixed arguments are made by various research groups on this matter. Some researchers made several attempts to exclude the use of catalysts in certain non-conventional processes. However, some other researchers are still in favor of catalytic route but with certain modification made to the production process. Recent development on efforts to accelerate biodiesel production process through non-catalytic routes is reviewed in the subsequent sections.

4. Non-catalyzed production of biodiesel

This section reviews two different non-catalytic biodiesel production process that have been reported in literature, i.e. supercritical and Biox processes. Specific process requirements and process behaviors are reviewed while respective drawbacks are highlighted.

4.1. Supercritical method

One of the approaches to overcome problems associated with poor immiscibility between the reactants and technical problems caused by catalysts is to use supercritical method. In this approach, no catalyst is involved. Supercritical alcohol transesterification reaction takes place under extremely high temperature and pressure. When a gas or liquid is exposed to pressure and temperature beyond its critical point, unusual phenomena on its properties are exhibited. Liquid and vapor phase are no longer confined under these conditions and single supercritical fluid phase is generated [13]. In the supercritical method, methanol and oil, which are immiscible liquids at room temperature will form a homogenous fluid. This is due to the sharp drop in the solubility of methanol and reduction in dielectric constant which makes methanol a non-polar substance [35]. Thus, the reaction is accelerated as no limitation with respect to mass transfer is expected under such conditions.

Tan et al. [36] investigated a one step supercritical method to produce biodiesel from palm oil under an optimum reaction temperature of 239 °C and a pressure of 8.1 MPa. Under these conditions, the highest biodiesel yield achieved was 70% in 20 min. On the other hand, Ilham and Saka [37] studied the production of biodiesel using Jatropha curcas oil using a two-step supercritical method. They reported that biodiesel 97% biodiesel yield was obtained in 15 min at 300 °C and 9 MPa.

Supercritical method is also not affected by FFA and no soap generation is involved because of the non-catalytic nature of the reaction. Therefore, the quality of biodiesel and glycerin is expected to be better than that for a catalyzed reaction and the reaction time is significantly low. Besides that, Supercritical method has high reaction rate so that the volume of the reactor can be significantly reduced [38]. Fig. 5 illustrates the typical flow diagram of a supercritical system for biodiesel production. It shows two stages of supercritical process where the separation of glycerol and recovery of the methanol are made in the respective stage.

Despite all the advantages, the main drawback of this method is that it depends on critical conditions of alcohol which demands high pressure (4.9–8.1 MPa) and temperature (239–290 °C) [39]. These requirements translate into high energy input for the process. Also, under such high temperature, the degradation of triglycerides cannot be avoided leading to undesired by-products formation that can affect the biodiesel quality. Besides safety considerations, the extreme reaction conditions also mean that the procedure is hard to be operated and requires specifically designed equipment. All these factors will negatively affect the overall process economy if an industrial scale of operation were to be considered. In closed systems, the reaction will also be shifted towards reversed reaction especially at high conversion due to the presence of more products in the reaction vessel [5]. This phenomenon will defeat the purpose of accelerating the reaction rate via supercritical method. As such, this method is deemed unsatisfactorily to address problems with respect to high net energy supply by biodiesel, mild reaction conditions and high product quality.

4.2. Biox process

Boocock et al. [40] developed a new technique named the Biox process to yield biodiesel non-catalytically with the use of

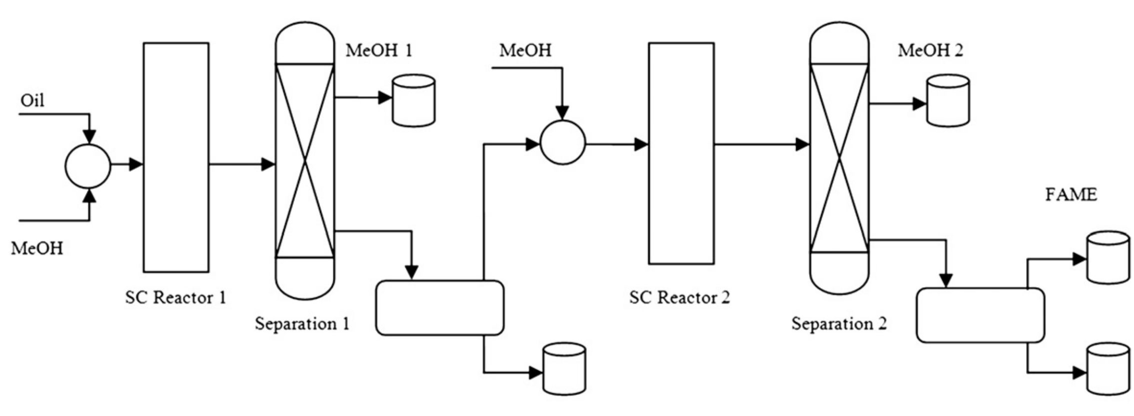


Fig. 5. Flow diagram of supercritical method for biodiesel production [34].

a co-solvent. The co-solvent was primarily used to overcome low solubility of methanol in oil. The process took place at a low temperature of 30 °C and it was able to convert oil with high percentage of FFA (more than 10%) into biodiesel in two steps. In the first step of the process, the conversion of FFA was achieved. The second step involved the conversion of triglyceride. The addition of the co-solvent was done in each step. Short reaction times of 5–10 min were recorded while the process was operated continuously for 90 min. The most common co-solvent to be used is tetrahydrofuran due to its close boiling point to that of methanol [13]. Fig. 6 describes the procedure where the reactor stage refers to individual stage involved while the separation of methanol and co-solvent is achieved in the lower separation process. The co-solvent is recycled and reused through the continuous process. In the separation process, both excess methanol and the co-solvent are recovered from the products.

The basic advantages of this process its ability to handle feeds with high FFA, the reaction time is short and it can be carried out under ambient temperature and pressure. The disadvantage of this process is that even though there is no catalyst present in the product phase, the co-solvent must be completely removed due to its hazardous and toxicity natures [19]. So this factor creates a big economical barrier as the separation of methanol and the co-solvent is difficult due to the very close boiling point of them. This difficulty can translate into added production cost while the residual solvent in the biofuel product can affect the compliance with the international standards [37].

As described above, a number of alternative approaches have been investigated to overcome problems faced in biodiesel production process. Each of the approaches has its own benefits and disadvantages. The following sections highlight another emerging technical approach to solve the problems. It involves the application of ultrasonic field to accelerate the process which is due to be carried out under mild reaction conditions. Fundamentals of its operation, the main advantages and drawbacks of this process will be thoroughly reviewed.

5. Ultrasonic energy and its industrial applications

This section provides some information of ultrasonic energy and its effects on liquid systems leading to its practical use in various industrial applications.

5.1. Introduction to ultrasonic energy

Ultrasound (US) is simply a sound pitch above human hearing ability i.e. usually above 20 kHz. It is a mechanical energy and has plenty of applications in our daily life [41]. The use of ultrasound as a source of energy is common these days and recently it is used to provide assistant to a great number of industries. Fig. 7 shows the general divisions of sound frequencies. The frequencies beyond 20 kHz till 100 kHz are used in industries but the range of industrially useful frequencies can only be extended to 2 MHz due to huge amount of energy needed to generate higher frequencies.

Ultrasound wave generates cavitation bubbles as it passes through the liquid [25]. Ultrasound wave travels like any other sound wave by a successive series of rarefaction and compression cycles vibrating the molecules of the carrier media, in this case the liquid reactants. When the attraction forces between the liquid molecules became less than the negative pressure of the cyclic rarefaction, a gap will be generated and is filled with vapor from the liquid. At the beginning of its lifetime, it begins tiny but within other successive cycles, it grows to form acoustic cavitation bubble.

5.2. Effects of ultrasonic on multiphase liquid systems

The use of ultrasonic energy in biodiesel production process is a new, attractive and effective procedure to solve problems that are faced by conventional methods. Ultrasonic irradiation can enhance mass transfer rate between the reactants which are immiscible liquids. It has been employed in a wide range of

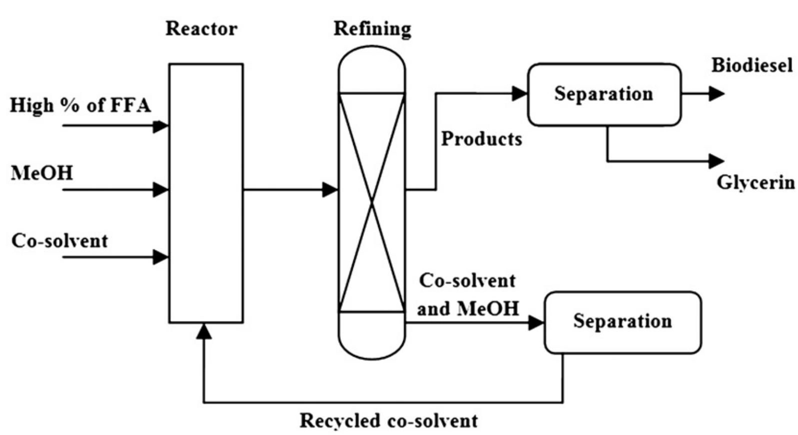


Fig. 6. Flow diagram of the Biox process.

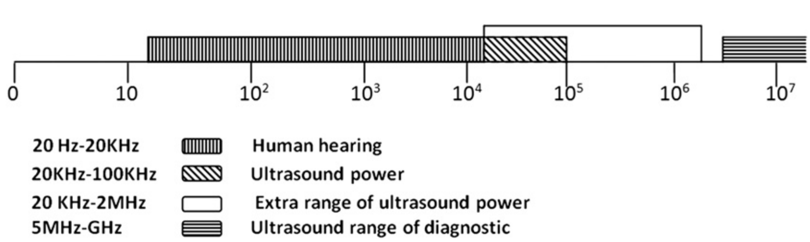


Fig. 7. General divisions of sound frequencies.

chemical processes causing reduction in reaction time and improvement in production yield [25]. Intensified reaction causes shorter reaction time, better product yield and lower catalyst requirement while supporting the use of greener heterogeneous catalysts. Mild reaction conditions translate into better process economy and simpler equipment set up.

Huge number of these bubbles can be generated in the liquid. Some of them are stable and can stand for another cycle while others will undergo vigorous breakdown once reaching certain critical size. The strong collapses generate local pressure in the order of 2000 atm and the temperatures could reach up to 5000 K [42]. It is shown in Fig. 8 that the bubbles are formed at zero time and undergoes breakdown after an approximate period of 400 μs. Small hotspots that are generated from these collapses can offer the energy for some chemical reactions. These phenomena result in severe mixing between the two immiscible liquids close to the phase boundary and force the liquids to inspire micro jets which can reach to a speed up to 200 m/s. The cause for the micro jets generation is the asymmetric breakdown of the cavitation bubbles [25].

One of the advantages of these cavitations is that it causes a local increase in temperature near the boundary layer and this increment will modify the course of the transesterification reaction that consequently offset the requirement for external heating in the production process. On the other hand, the formation of micro jets eliminates the need for intense mechanical agitation to improve mass transfer between the two reactant phases [42]. Ultimately, significant improvement in the reaction rate will result.

5.3. Industrial usages of ultrasonic energy

During 1920s, the earliest use of acoustic waves to generate cavitations to significantly change the reaction rate was attempted. During 1940s, many efforts were done to use ultrasound in polymer manufacturing and chemical processing [43]. No further progress in this topic had been made until 1970, where many successful applications were achieved. In 1960s, the development began after the spread of commercial ultrasonic devices in laboratories of chemistry, biology and metallurgy [44]. In the recent years, ultrasonic irradiation attracted researchers to incorporate it in many new areas such as manufacturing of nanostructured materials [45,46], food industry [47–49], sonodynamic therapy [50–52], processing of biomass [53,54] and sonochemical degradation of pollutant materials and hazardous chemicals [55–57].

A low frequency ultrasonic-assisted system can be used to produce emulsions from immiscible liquids [58–60]. As the feeds for biodiesel production process are immiscible, ultrasonication could be beneficial for transesterification of triglyceride with alcohol and early successes have been reported [61,62]. Besides reduction in reaction time and catalyst requirement, ultrasonic-assisted transesterification also minimizes alcohol to oil molar ratio and limits energy consumption [62]. As such, the objective of achieving better net energy from the biodiesel will be achieved. Mild reaction conditions at short reaction time also mean lower opportunity for the occurrence of undesired side products leading to better quality of the biodiesel product [61].

6. Batch biodiesel production process

This section reviews various biodiesel production processes using batch reactor system. The use of various base and acid catalysts in conventional and ultrasonic-assisted reactor system is compared and properly discussed.

6.1. Introduction

Early attempts on the study of vegetable oils transesterification under ultrasonic field were made using batch process. This process mode is easy to deal with and the control of reaction temperature can be made with the use of appropriate technique (like water bath) [63,64]. In the conventional reactor set up, vigorous agitation process in the reactor is done using a suitable mechanical agitator (magnetic stirring in the case of small scale study or anchor type agitator). Investigation on a batch process to use ultrasonic irradiation instead of mechanical stirring has been made using ultrasonic horn or probe that is immersed in the reaction media [64]. Fig. 9 shows a schematic diagram of ultrasonic-assisted batch reactor system for biodiesel production. It can be seen that the catalyst and the desired alcohol are mixed in pretreatment stage before the reactor. The ultrasonic probe provides the reactor with ultrasonic energy followed by phase separation stage. During the phase separation stage, the product can be collected while the remaining residue can be further separated to extract the catalyst and glycerin. In this study, the review on an ultrasonic-assisted batch reaction system will be divided into homogenous and heterogeneous catalysts. Major highlights to the process behaviors and behaviors are also given in the following sub-sections.

6.2. Biodiesel production process using homogenous catalyst

Production of biodiesel using homogenous catalyst has been investigated by many researchers using conventional batch process. Catalysts such as potassium hydroxide [65], sodium hydroxide (NaOH) [29] and other types of homogenous catalysts [66] have been studied. Compared with other types of catalyst, homogenous catalysts generally attract researchers' attention and widely used in industries. Table 2 summarizes the use of these catalysts under conventional conditions. It could provide high conversion but the reaction time to achieve high yield is large, especially in the case of H_2SO_4. Typically, yields higher than 95% are only possible between 120–180 min. Reaction temperatures also vary but if higher than 65 °C is needed, pressure reaction should be used as methanol will evaporate beyond that temperature which is its boiling point [67].

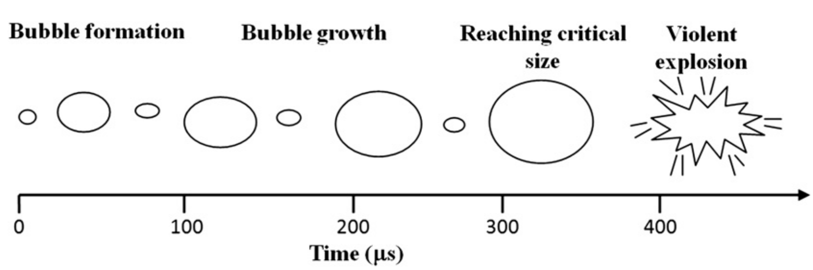


Fig. 8. Formation, growth and collapse of a cavitation bubble.

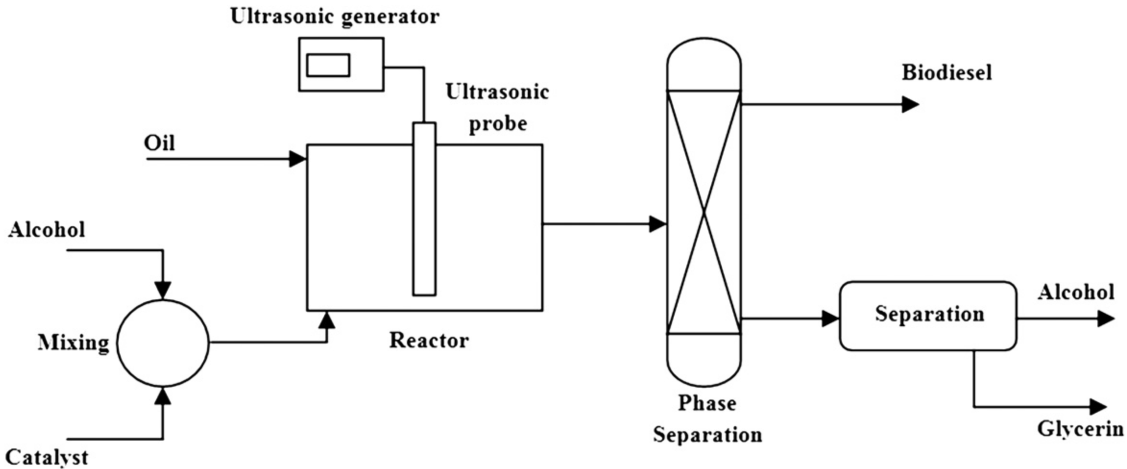


Fig. 9. Basic scheme for ultrasonic batch biodiesel production.

Table 2
Performance of various homogenous catalysts in biodiesel production process using conventional stirring reaction system.

Feed oil	Catalyst	Reaction conditions					
		Alc:oil[a]	W_{cat} (w/w_{oil})	Temperature (°C)	Time (min)	Biodiesel yield (%)	Reference
Rapeseed	KOH	6:1	1	65	120	96.0	[68]
Used frying oil	KOH	7.5:1	1.1	70	30	86.0	[69]
Sunflower	NaOH	6:1	1	60	120	97.1	[70]
Waste cooking	H_2SO_4	20:1	4	95	600	90.0	[31]
Soybean	H_2SO_4	3:1	3	120	60	> 95.0	[5]
Waste cooking	$Fe_3(SO_4)_2$ followed by CaO	7:1	Acid: 0.4	60	180	81.3	[62]
			Base: -	60	180		

[a] Alcohol to oil molar ratio.

Table 3
Performance of ultrasonic-assisted reaction system for biodiesel production using various homogenous catalysts.

Feed oil	Catalyst	Reaction conditions						
		Alc:oil ratio	Frequency (kHz)	W_{cat} (w/w_{oil})	Temperature (°C)	Time (min)	Biodiesel yield (%)	Ref.
Soybean	KOH	6:1	20	1.5	25, 40, 60	15	99.4	[71]
Triolein		6:1	40	1	30–50	30	Vary	[72]
Coconut		6:1	24	0.75	–	7	98	[80]
Waste cooking oil		6:1	20	1	45	Up to 40	Vary	[64]
Sunflower		7.5:1	40	0.7	32.2	60	88	[74]
Soybean	NaOH	9:1	40	0.2	29	30	100	[75]
Sunflower		7:1	24	2	Meth: 60	20	95	[29]
					Eth: 80	40	98	
Soybean		6:1	Ultrasound + microwave	1	60	3	97.7	[77]
Palm fatty acid distillate	H_2SO_4	7:1	22	5	40	150	90	[78]
Oreochromis niloticus	H_2SO_4 + KOH	9:1	40	2	30	90	98.2	[79]

6.2.1. Homogeneous base-catalyzed process

Recent works on the use of ultrasonic to accelerate biodiesel production process using homogeneous catalysts are summarized in Table 3. It is noted that generally high biodiesel yields (> 95%) were achievable in less than 60 min. In investigating the effect of reaction temperature on production process under ultrasonication, Colucci et al. [71] used soybean oil as the feed to react with methanol and the reaction was catalyzed by KOH. Three levels of temperature, i.e. 40 and 60 °C were carefully studied and high yield of above 90% was achieved at each level in just 15 min. They attributed the high reaction rate to the increase in the interfacial area between the reactants that resulted from cavitation bubbles generated by ultrasonic irradiation. This phenomenon allowed efficient contact between the catalyst and the reactants. Another trial to investigate the optimum reaction temperature was made by Hanh et al. [72] by testing the ultrasonic-assisted transesterification of triolein using KOH as catalyst. The tested temperature was in a range between 30–50 °C. They reported that the concentration of the product increased drastically with increasing temperature.

The use of other feed stock as a source of triglycerides for transesterfication process has been attempted by Teixeira et al. [73]. Beef tallow was used instead of vegetable oil while KOH was used as the catalyst. They concentrated on this type of feed stock due to its low price, highly produced in slaughters and other economic benefits. The results showed that short reaction time was achieved through ultrasonication leading to a reduction in the effects of free fatty acids content in fats even with the use of alkali catalyst. After collecting the results from conventional and

ultrasonic processes, no clear difference was noticed on the yield of biodiesel. Probably, it was due to near equilibrium operation of those systems at high conversion so that difference in the yields at the end of the reaction was not so significant.

Another different type of feed stock was studied by Hingu et al. [64]. They used waste cooking oil and methanol in the production process. A sonochemical reactor was used for studying different parameters affecting the transesterification process. Optimization was subsequently made to identify the optimum conditions and to compare the obtained results with those of conventional mechanically stirred reactor. The same researchers also investigated the ultrasonic rated power dissipation and found that under a power of 200 W, the conversion reached about 89% in less than 40 min. It was mainly attributed to the effect of ultrasound mixing. However, the conversion suffered a decrease when the power was increased to 250 W. That could be associated with the cushioning effect which, in turn, decreased the cavitational activity due to the reduction of the transferred power into the system. Some researchers also studied the effect of ultrasound pulse and found that higher conversion was obtained when ultrasound duration in the pulse was higher. The period between the pulses is important because it reduces the energy consumption and provides a period of cooling for the transducers [43].

Three parameters of reaction variables under ultrasonication were studied by Avramovic et al. [74]. Levels of methanol-to-sunflower oil molar ratio, KOH catalyst loading and the temperature of reaction were subsequently optimized. The most significant factor on the production process was found to be the loading of the catalysts. They explained that the increase in catalyst loading resulted in an increase in the formation of methoxide (the complex formed from the reaction between catalyst and methanol). This yielded an enhancement in the FAME formation and an increment in the positive catalyst affect on the rate constant of the forward reaction. A yield of nearly 90% was achieved in just 60 min.

Another type of homogenous catalyst has been successfully used in conjunction with an ultrasonic system. Santos et al. [75] converted soybean oil to biodiesel by reacting it with methanol catalyzed by NaOH. The methanol to oil ratio was influential in governing the final biodiesel yield. That was because the use of higher concentration of alcohol shifted the reaction equilibrium toward the products. Nearly 100% yield was achieved in just 30 min. Meanwhile, the use of large amount of catalyst under the optimum methanol to oil ratio caused the intensification of side reactions like soap formation. As such, ultrasonication can possibly improve this process on the basis of a reduction in the required amount of the catalyst.

On the other hand, Georgogianni et al. [76] compared the use of homogenous and heterogeneous catalysts with the presence of ultrasonic waves and under mechanical stirring using rapeseed oil as feed. They found that homogenous catalyst (NaOH) was more active than the other heterogeneous catalysts (Mg-MCM-41, Mg–Al hydrotalcite, and K-impregnated zirconia). They attributed the difference to the diffusion limitations of the bulky oil molecules into the tiny pores of the solid catalysts. The beneficial role of ultrasonic irradiation was demonstrated as a significant reduction in the reaction time for the homogenous catalyst.

Combining both effects of ultrasonic and microwave irradiation was attempted by Hsiao et al. [77] with the intention of achieving optimal ultrasonic mixing and microwave irradiation effects. The conversion of soybean oil with the presence of NaOH was made in two discrete steps. The first step was assisted by ultrasonic mixing while maintaining the temperature near room temperature for one minute. It was followed by the reaction with the assistance of microwave irradiation for 2 min. They recorded that this procedure did not require mechanical stirring and cooling facility. Evaporation of alcohol was also significantly lower and reduced energy consumption resulted due to low reaction temperature requirement. Thus the use of ultrasonic field in combination with microwave looks very promising for biodiesel production.

Recent research findings confirmed that the use of these homogeneous catalysts in combination with ultrasonication is effective, time saving and economical method for producing biodiesel from different types of feed stock [18]. In short, the use of ultrasonic-assisted process could lead to high yields in short reaction time, low reaction temperature and reduce the amount of hydroxide catalysts needed. Beside hydroxides, other type of catalyst to be possibly used is liquid acid catalyst which is especially useful for feed stock with high free fatty acid (FFA) content.

6.2.2. Homogenous acid catalysts

The search for cheap and effective raw material for biodiesel production has been attempted by Deshmane et al. [78]. They used palm fatty acid distillate (PFAD) which is usually a much cheaper raw material compared to vegetable oils in the esterification reaction with methanol. They used concentrated H_2SO_4 catalyst due to its insensitivity to FFA. The researchers investigated the effect of various reaction parameters to reach the optimum conditions. They reported that significant effect of ultrasonic field was achieved at only 40 °C with 90% yield in 2.5 h. The reaction time was much shorter than that reported by Wang et al. [31] using a non-ultrasonic reactor system. They attributed the positive effect to the improved mass transfer rate between the reactants that governed the whole process.

Ultrasonic-assisted process can be also used in two-stage biodiesel production process using feed stock with high FFA content as reported by Santos et al. [79]. They used Oreochromis niloticus (Nile tilapia) oil with methanol using two types of catalysts sequentially. The first catalyst was KOH which reacted with oil in alcoholic saponification process in a single stage followed by an acid hydrolysis step catalyzed by sulfuric acid. After the first stage of the process, acid catalyst was added to the reaction mixture to complete the reaction using ultrasonic irradiation in each step. The researchers also used response surface methodology (RSM) to predict the effects of three of reaction parameters on the biodiesel yield. These parameters were alcohol to oil ratio, sulfuric acid concentration and reaction temperature. It was found in this study that the most important parameter was alcohol to oil ratio because it shifted the equilibrium towards the products side. The results also showed that the application of ultrasonic waves neglected the need of external heating and ultrasonic irradiation had a positive influence on the yield of methyl esters. In their study, a yield of 98% was achieved in just 1.5 h.

6.3. Heterogeneous catalysts

The use of homogenous catalyst has been reported to be successful in the production of biodiesel using ultrasonic technique. However, homogeneous catalysts cannot be reused because they are consumed in the reaction media and the separation process of this type of catalyst is difficult and requires further equipment. These factors can affect the overall process economy and energy consumption [24]. As such, efforts have been recently dedicated to the investigation using heterogeneous catalyst that can achieve the same level of efficiency while providing opportunity for catalyst reuse. For comparison, findings from studies using conventional stirring reaction and ultrasonic-assisted reactor system are reviewed in the next section.

6.3.1. Conventional production using heterogeneous catalysts

Alkaline earth metal oxides, especially CaO and SrO have received much interest due to their relatively high basic strength,

low solubility in reaction media and relatively cheap prices [81–82]. Another type of alkali catalyst that has also been investigated and reported is potassium catalyst supported on SBA-15 [83]. Alkali catalysts could suffer when high concentration of FFA is present in the oil. Therefore, many types of metal oxide catalysts [84] or heterogeneous acid catalysts have been examined such as zirconium oxide (ZrO_2) [85], sulfonic ion-exchange resin [86–87], sulfonic modified silica [26,27] and heteropoly acids (HPAs) [88,89]. Some of the research works utilizing heterogeneous catalyst systems in conjunction with conventional mechanically stirred production process are summarized in Table 4. It is clear that these catalysts could provide high yields but they required long reaction time. Reaction temperatures were moderate except for the sulfonated SBA-15. For all reactions, the molar ratios of alcohol to oil ratio were high compared to the ratios of homogenous catalysts under similar conditions. Whereas high alcohol to oil ratio was needed to shift the equilibrium to the products side, it also resulted in the dilution effect on the oil concentration leading to poor rate of reaction [28].

In fact, there are some other limitations to the successful use of heterogeneous catalyst. One of the limitations is the formation of three phases in the reaction media (oil, methanol and catalysts) which can also cause a reduction in the rate of reaction. One of the solutions to this problem is to use a certain quantity of co-solvent to enhance the miscibility of oil and methanol [94]. However, the other way and the most effective is still the use of ultrasonic-assisted process.

6.3.2. Heterogeneous catalysts under ultrasonic conditions

Reaction parameters and results of some studies that are focused on the use of heterogeneous catalysts in conjunction with ultrasonication are summarized in Table 5. As concluded from this table, the yields of biodiesel achieved were generally high and comparable with those of homogenous catalysts. However, the reaction temperatures were slightly higher while the reaction times were longer. Catalyst loading under ultrasonic field is usually higher than that for homogenous catalysts but this does not significantly affect the economics of the process due to its simple separation process.

Production of biodiesel from palm oil using BaO and SrO as the heterogeneous catalysts has been performed by Salamatinia et al. [95]. They used ultrasonic-assisted process to enhance reaction rate and to study the effects of ultrasonic waves on the reaction parameters. They reported that the basic properties of the catalyst were the main cause for their high activity. The results showed that the low frequency ultrasonic-assisted process had no significant mechanical effects on SrO but there was some effects on BaO. This study confirmed that the ultrasonic significantly improved the process by reducing the reaction time to less than 50 min at a catalyst loading of 2.8 wt.% to achieve biodiesel yields of above 95%. The optimum alcohol to oil ratio was found to be at 9:1.

Another study on alkali earth metals was done by Mootabadi et al. [96]. The researchers investigated the effect of ultrasonic waves at 20 kHz and 200 W on the regenerated catalyst and made comparison between mechanical stirring and ultrasonic irradiation. They used palm oil in the production process and investigated the optimum conditions for the catalysts (CaO, SrO and BaO). Ultrasonic irradiation showed great enhancements on the reaction parameters for the ultrasonic-assisted process, especially for the obtained yield and reaction time. It was concluded that catalyst leaching was the main cause for the drop in activity in the case of regenerated catalyst. BaO catalyst was the least stable to leaching. Under the optimum conditions, 95.2% yield was achieved in just 60 min of reaction for both BaO and SrO catalysts while that of for CaO was only 77.3%. These results were about 30–40% higher than the corresponding results obtained using conventional stirring reactor system.

Table 4
Performance of various heterogenous catalysts in biodiesel production process using conventional stirring reaction system.

Feed oil	Catalyst	Reaction conditions					
		Alc:oil ratio	W_{cat} (w/w_{oil})	Temperature (°C)	Time (min)	Biodiesel yield (%)	Ref.
Soybean	CaO	12:1	8	65	3	95.0	[90]
Soybean	KOH/NaX Zeolite	10:1	3	65	8	85.6	[91]
Waste frying oil	Novozyme 435	25:1	10	50	4	89.1	[16]
Palm	KF/ZnO	11.43:1	5.52	65	9.72	89.2.	[92]
Soybean	KI/Mesoporous silica	-	5	70	8	90.1	[93]
Palm	Sulfonated SBA-15	20:1	6	140	4	95.0	[27]

Table 5
Performance of ultrasonic-assisted reaction system for biodiesel production using various homogenous catalysts.

Feed oil	Catalyst	Reaction conditions						
		Alc:oil ratio	Frequency (kHz)	W_{cat} (w/w_{oil})	Temperature (°C)	Time (min)	Biodiesel yield (%)	Ref.
Palm	BaO SrO	9:1	20	2.8	65	~50	>95.0	[95]
Palm	BaO	9:1	20	3	65	60	95.2	[96]
	SrO						95.2	
	CaO						77.3	
Jatropha curcas	Na/SiO_2	9:1	24	3	Low	15	98.5	[97]
Soybean	Immobilized Novozym 435	6:1	40	6	40	240	96.0	[98]
Frying oils	Mg-MCM-41, Mg–Al hydrotalcite, K/ZrO_2	-	24	-	60	300	>95.0	[99]

To study the performance of an immobilized catalyst, Kumar et al. [97] prepared a supported Na/SiO_2 catalyst to investigate the effects ultrasonication on the process. Under the optimum conditions and with the use of Jatropha curcus oil as feed stock, they managed to achieve 98.5% of biodiesel yield in just 15 min of reaction time. They found that the use of ultrasonic-assisted process reduced the amount of catalyst that must be used in the process. They attributed that finding to the effects of ultrasonic cavitation on increasing the surface area available for the reactants. That, in turn, increased the activity of the catalyst even at minimum catalyst dosage. As a result, the purity of glycerol which is the main by-product of biodiesel production was increased. The researchers also investigated the reusability of the catalyst and found that after five cycles, the reaction conversion showed minimal reduction.

Another attempt to produce biodiesel from soybean oil was made by Yu et al. [98] by combining the use of different types of catalyst known as Novozym 435 (Candida Antarctica lipase B immobilized on polyacrylic resin). The procedure involved the combination between the effects of ultrasonic waves and mechanical vibration instead of mechanical stirring due to its detrimental effects on the catalyst. The researchers studied the effects of reaction parameters on the activity of the catalyst. The catalyst showed good stability with no loss of enzymatic activity after five successive cycles under ultrasonic irradiation. In spite of slightly longer reaction time, high production yield was obtained at low reaction temperature.

Other types of heterogeneous catalysts were used in the work of Georgogianni et al. [99]. They investigated a wide range of catalysts including Mg-MCM-41, Mg–Al hydrotalcite, and K^+-impregnated zirconia. The bases of selection for these catalysts were mesoporosity and surface basicity. The reaction mixture consisting of frying oils, methanol and the desired catalyst was mixed in a batch reactor via mechanical stirrer for 24 h or via ultrasonicaion for 5 h. The results suggested that the basic strength was the cause of the good activity of the catalysts. Mg–Al hydrotalcite achieved the highest reaction conversion of 97% at a reaction temperature of 60 °C. Thus, ultrasonic irradiation significantly enhanced the reaction rate causing a reduction in reaction time.

Comparison between the parameters of reactions listed in Table 5 under ultrasonic field with those in Table 4 for conventional mechanical stirring processes for heterogeneous catalysts clearly shows the enhancements caused by ultrasonic irradiation. Reaction times and catalyst loadings of the ultrasonic-assisted processes were shorter than those for the conventional processes. The molar ratios were less than those of conventional processes and the production yields were higher. As a conclusion, with the use of ultrasonic, high activity of homogenous catalysts can be achieved using the more environmental friendly heterogeneous catalysts.

6.4. Performance of different alcohols under ultrasonic field

Many efforts have been dedicated to investigate the influence of the type of alcohol that is used for biodiesel production under ultrasonic irradiation [80,100,101]. The use of ethanol was attempted by Kumar et al. [80]. They used coconut oil catalyzed by KOH to be reacted with the ethanol to produce biodiesel. It was reported that the justification for the use of ethanol was to reduce the hazard associated with the use of methanol which is highly toxic in the batch process. Ethanol has also more carbon atoms which could provide higher colorific value. However, transesterification using ethanol has been reported to be slightly lower due to its larger molecular size [100]. They compared the results of the production using ultrasonic irradiation with that of conventional stirring to show the differences. Reaction time was found to be reduced by 15–40 times compared to that of mechanical stirring. They also investigated the effects of ultrasonic pulse and amplitude to optimize the yield. It was concluded that the optimum pulse and amplitude were 0.3 s and 60%, respectively. The relatively short reaction time of this process was a good indication of the positive role of ultrasonication in enhancing the process using ethanol.

Other researchers [100] studied the effects of ultrasonication on esterfication process involving short chain alcohols (ethanol, propanol, and butanol) reacted with oleic acid to produce corresponding fatty acid ethyl esters (FAEEs). They used batch esterification process to optimize the reaction parameters using H_2SO_4 as an insensitive catalyst to the presence of FFA. They reported that ultrasonic condition was effective, economic, and time saving in the esterification process, regardless of the type of alcohol used.

The use of different types of alcohol that can be used in conjunction with ultrasonication using common types of alkali catalyst, i.e. KOH and NaOH has also been investigated by Hanh et al. [101]. They discriminated a wide variety of alcohols including methanol, ethanol, propanol, butanol, hexanol, octanol and decanol. The desired alcohol was used to react with triolein oil in the presence of KOH or NaOH. They comparatively investigated the use of both ultrasonic irradiation and mechanical stirring in the reaction. It was found that the type of alcohol had great influence on the yield. It was concretely revealed that the rate of the reaction depended on the type of alcohol. In other words, as the number of carbon in alcohol increases, the rate of the ester formation decreases. That is because alcohol with large number of carbon makes it difficult to separate ester from the unreacted oil. In this respect, it was proven that ultrasonic irradiation could enhance the rate of biodiesel formation using short-chain alcohols as compared to that achieved with conventional mechanically stirred system.

A study on the effects of primary, secondary and tertiary alcohols on the reactant's conversion with the aid of NaOH has been made by Stavarache et al. [62] who examined these types of alcohol for reaction under the effect of ultrasonication. The results showed that normal straight chain alcohols were more reactive. It could achieve 98–99% of conversion under optimum conditions while relatively lower conversion could be achieved using secondary and tertiary alcohols under the same conditions. They attributed that observation to the steric hindrance that hampered or limited the access towards the centre of the reaction and caused lower reaction rate. It was found that low frequency ultrasonication at around 28 kHz could result in a higher conversion but the reaction took longer time than those achieved at high frequencies. However, too high frequencies were not useful at all for the production of biodiesel because the collapses of cavitation bubbles were weaker than impinging of one reactant to the other [101].

Thus, it can be concluded from Table 6 that ultrasonic irradiation can be successfully used to accelerate the reaction with other types of alcohols. Better yield can generally be achieved with primary alcohols and reasonable reaction time and temperature can be used. It is noted that for transesterification process, the reaction temperature and time were less influential than those in esterification process when sulfuric acid was used as the catalyst while the yields of biodiesel of transesterification processes were relatively higher.

7. Continuous process under ultrasonic field

The use of ultrasonic-assisted batch process in the production of biodiesel has been discussed and effects of various reaction parameters have been investigated. Batch process has several

Table 6
Performance of ultrasonic-assisted biodiesel process using various types of alcohol.

Feed oil	Catalyst	Reaction conditions						
		Alc:oil ratio	Frequency (kHz)	W_{cat} (w/w_{oil})	Temperature (°C)	Time (min)	Biodiesel yield (%)	Ref.
Coconut	Ethanol	KOH	6:1	0.75	–	7	98%	[80]
Oleic acid	Ethanol, propanol butanol	H_2SO_4	3:1	5	60	120	> 90%	[100]
Triolein	Wide range	NaOHKOH	6:1	1	25	60	> 90%	[101]
Commercial edible oil	Primary, secondary and tertiary	NaOH	6:1	0.5	Room	10–20	98–99%	[62]

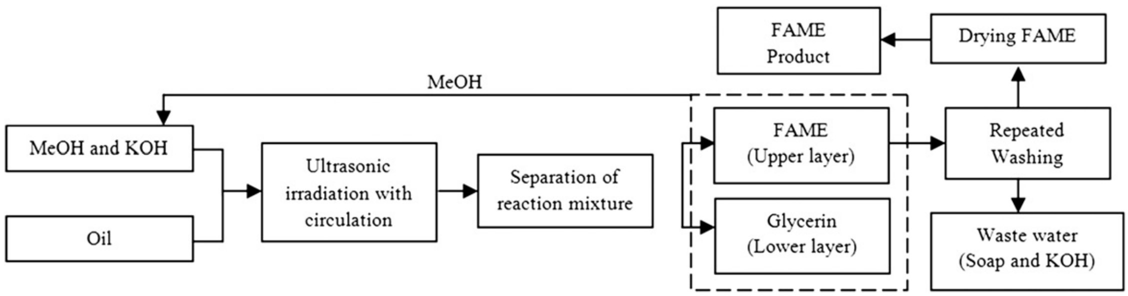


Fig. 10. Flow diagram of ultrasonic-assisted process for biodiesel production [104].

disadvantages, especially when used in large scale. Drawbacks in the batch process such as the requirement of larger reactor, low efficiency due to its start up and shut down requirements and high labor costs will affect the process economics [102]. For these reasons, researchers have tried to study continuous systems provided with ultrasonic irradiation to tackle these problems and to find suitable procedure that can satisfy various needs in biodiesel production. The investigations in the area of continuous systems for biodiesel production should be further developed towards large scale continuous processes [103].

The design of a pilot plant for continuous production of high quality biodiesel has been attempted by Thanh et al. [104]. The pilot scale plant was designated to perform the transesterification in a circulation process in the presence of low-frequency ultrasound. KOH was used as the catalyst to transesterify canola oil and methanol. Using liquid pumps, oil and methanol containing the dissolved catalyst were fed into the ultrasound reactor passing to circulation-separation unit. After that, feeding valves were closed and circulation valves were opened to circulate reaction mixture through the reactor. After this stage, the reaction mixture was left to undergo phase separation in the circulation-separation unit for 4 h. The flow diagram that describes the circulation process is shown in Fig. 10. The aim of the researchers was to produce biodiesel that satisfied several objectives including material saving and low energy consumption. They concluded that one of the advantages of ultrasonic field was the reduction in energy consumption for the whole process. However the use of this method could be just limited to homogenous catalyst.

Design and operation of continuous process assisted by ultrasonic irradiation have been studied by Stavarache et al. [105]. They investigated the effects of various types of vegetable oils and alcohol to oil ratios. The influences of parameters of the continuous process such as reaction volume and residence time of the reactants inside the reactor were particularly investigated. The catalyst used was KOH and the oils were palm oil and commercial edible oil while reaction temperatures were between 38–40 °C. The reactor was initially filled by pumping the reactants of a desired ratio. During the first loading, ultrasound was turned off. After that, the reaction was started in a batch mode for durations equal to the selected residence times. After that, the pumps were started and the reaction was turned to continuous mode for twelve successive volumes. From the results obtained, the researchers proved that ultrasonic irradiation was also suitable for a large-scale continuous transesterification of vegetable oil.

Another study with different type of oil processed using two-step continuous system was made by Thanh et al. [106] and schematically shown in Fig. 11. Waste cooking oil and KOH dissolved in methanol were pumped at a desired ratio to the first reactor where ultrasonic irradiation was provided. The reaction mixture flow rates were kept between 0.5–2.5 L/min. After that, the mixture was fed into a separation unit where phase separation took place. The upper layer that contained FAME, triglyceride and amounts of diglyceride and monoglyceride were fed to the second reactor which was also provided with ultrasonication. As in the first stage, the second one was followed by phase separation unit to collect the final product of FAME. This final product was then sent to a purification unit to extract the remaining catalyst and the excess of methanol. Short residence times of less than one minute were recorded for each reactor but the total time for the whole process was about 15 h due to long time required in the separation units. It was clear from the results of this work that an ultrasonic-assisted continuous system was a plausible and interesting technique for the production of biodiesel from waste cooking oil.

In Table 7, it can be concluded that ultrasonic irradiation can be successfully used in continuous processes as well as for batch processes. The yields of each continuous process were high enough to encourage researchers to further investigate this topic. However, early success in the continuous mode was only achieved using homogenous catalysts. Thus, further investigation should be dedicated to the use of heterogeneous catalysts under continuous operation. Certainly, the involvement of heterogeneous catalysts will require additional technical enhancements.

8. Conclusions

Biodiesel is a renewable, clean and alternative fuel to petroleum diesel. For all the possible methods for biodiesel production, catalytic transesterification of vegetable oil or animal fats with alcohol is the best method with good quality product. However, the production process faces many drawbacks related to the

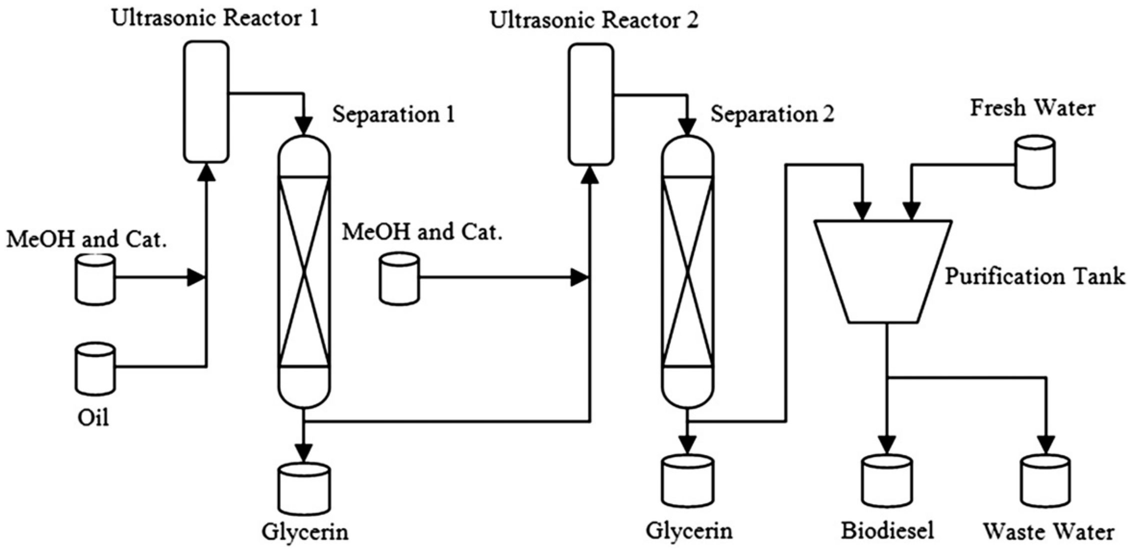


Fig. 11. Flow diagram of two-steps continuous process for biodiesel production [106].

Table 7
Performance of various continuous system of ultrasonic-assisted biodiesel production process.

Process	Feed oil	Catalyst	Reaction conditions						
			Alc:oil ratio	W_{cat} (w/w_{oil})	Temperature (°C)	RT[a] (min)	Rate (L/min)	Yield (%)	Reference
Circulation process	Canola	KOH	5:1	0.7	Room	40	8	99	[104]
Continuous process	Palm	KOH	6:1 and 7.5:1	–	38–40	20	–	∼90	[105]
Two stage continuous process	Waste cooking oil	KOH	1st stage 2.5:1	1st stage 0.7	Room	1	1st stage 1.5	1st stage 81	[106]
			2nd stage 1.5:1	2nd stage 0.3	Room	1	2nd stage 2	2nd stage 99	

[a] RT: Residence time.

immiscible nature of the reactants and the presence of free fatty acids in the desired oil. Several approaches have been proposed but only to a limited success. Heterogeneous catalysts which are more environmental friendly usually subject to a drawback of low catalytic activity. Ultrasonic irradiation has been proven to be successfully used in a meaningful way to enhance the emulsification of the reactants to increase the mass transfer rate during the reaction. This enhancement leads to reductions in reaction time, catalyst amount, alcohol-to-oil ratio and reaction temperature causing a significant decrease in the production economics. Ultrasonic irradiation was tested for wide range of homogenous and heterogeneous catalysts and showed promising results on the reaction variables compared with the results of conventional process. Mature understanding on the ultrasound-assisted transesterification process catalyzed by heterogeneous catalysts is yet to be established. However, there have been preliminary few attempts to elucidate the specific behaviors of the process with different types of alcohol, different types of solid catalyst as well as the effects of critical process variables such as temperature, catalyst loading, reactants' ratio etc. Thus, mature understanding on the use of ultrasonic energy to accelerate the transesterification process could be of great future interest for both batch and continuous production systems towards a more sustainable biodiesel production process.

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